Optical Transitions in Highly Charged Californium Ions with High Sensitivity to Variation of the Fine-Structure Constant

J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong
School of Physics, University of New South Wales, Sydney, New South Wales 2052, Australia
(Received 2 April 2012; published 16 August 2012)

We study electronic transitions in highly charged Cf ions that are within the frequency range of optical lasers and have very high sensitivity to potential variations in the fine-structure constant, α. The transitions are in the optical range despite the large ionization energies because they lie on the level crossing of the $5f$ and $6p$ valence orbitals in the thallium isoelectronic sequence. Cf^{16+} is a particularly rich ion, having several narrow lines with properties that minimize certain systematic effects. Cf^{16+} has very large nuclear charge and large ionization energy, resulting in the largest α sensitivity seen in atomic systems. The lines include positive and negative shifters.

DOI: 10.1103/PhysRevLett.109.070802 PACS numbers: 06.30.Ft, 31.15.am, 32.30.Jc

Introduction.—In this Letter, we present calculations of transitions in highly charged californium that could form the reference for an optical atomic clock with very strong sensitivity to variation of the fine-structure constant, $\alpha = e^2/\hbar c$. Our work is motivated by recent astronomical studies of quasar absorption spectra that indicate a spatial gradient in values of α across cosmological distances [1,2]. The results were taken using around 300 spectra covering most of the sky, observed at two telescopes: the Very Large Telescope in Chile [2] and the Keck Telescope in Hawaii [3–5]. The telescopes independently agree on the direction and magnitude of the gradient (dipole), which is significant at 4.2σ for the combined sample of both telescopes.

The cosmological dipole in α might be confirmed by terrestrial studies, since the solar system is moving with respect to the cosmic microwave background (the presumed frame for the α dipole), and therefore should be moving from a region of the Universe with smaller values of α to one with larger values [6]. In particular, the expected rate of change in α today would be of order $\dot{\alpha}/\alpha \sim 10^{-18}$ yr^{-1}. This is significantly smaller than the best current terrestrial limits, $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17}$ yr^{-1}, which comes from comparison of Al^+ and Hg^+ atomic clocks [7]. If measured at the same level of accuracy, the transitions proposed in this work would allow an improvement on this limit by a factor of 23. Because the transitions have narrow natural linewidths and reduced systematics, the improvement could be even larger.

We parametrize the sensitivity of an atomic transition to potential variation in α by the quantity q defined by

$$q = \left.\frac{d\omega}{dx}\right|_{x=0}, \tag{1}$$

where $x = \alpha^2/\alpha_0^2 - 1$ is the fractional change in α^2 from its current value α_0^2 and q and ω are measured in atomic units of energy. In the Al^+ and Hg^+ comparison, the Al^+ clock is an "anchor" (relatively insensitive to α variation) whereas the mercury clock has a strong sensitivity of $q = -52\,200$ cm^{-1} [8]. An approximate formula for the q value of a single energy level ($E_n = -I_n$ where I_n is the ionization energy of the level) with effective principal quantum number ν and angular momentum j is [9,10]

$$q_n \approx -I_n \frac{(Z\alpha)^2}{\nu(j+1/2)}, \tag{2}$$

where Z is the nuclear charge. The transition will have a sensitivity to α variation that is the difference between the q values of the levels involved. Therefore, the best transitions will maximize the difference of ν and j between the levels and will come from heavy ions.

Equation (2) shows that transitions in highly charged ions (HCIs) can have much larger q values since they have much larger ionization energies. Unfortunately, they generally also have much larger transition energies, putting them outside the range of optical lasers and making them unsuitable for use in high-precision clocks. However, due to configuration crossing, some HCIs can have optical transitions between levels with different principal quantum numbers, and these could become reference transitions for optical clocks with the highest q values seen in atomic systems [10,11].

An alternative enhancement mechanism comes from comparison of closely spaced excited levels. For example, neutral dysprosium has two excited levels that are nearly degenerate and have q values of different signs. Therefore, transitions between these two levels have high relative sensitivity to α variation, $K = 2\Delta q/\omega \sim 10^8$ [12–14], despite the q values themselves being $\sim$100 times smaller than those of the current work. Unfortunately, one of the states is quite broad, and this limits the accuracy. The excited spectra of helium-like ions can also have level crossings in excited states with large K values [15]; however, again the transitions are relatively broad.

In this Letter, we further advance the search for HCIs suitable for the study of α variation. We present calculations for the $5f - 6p_{1/2}$ crossing that occurs in the thallium and lead isoelectronic sequences (with one valence electron and two valence electrons, respectively). The crossing occurs at $Z = 98$—californium—which also happens to be one of the last relatively stable ions in the periodic table that can be produced in macroscopic quantities, having isotopes with half-lives of several hundred years. To improve limits on α variation requires either increasing signal (larger q) or decreasing systematics. The Cf^{16+} ion does both. First, due to a higher Z value, the transition frequencies of the Cf^{17+} and Cf^{16+} ions are much more sensitive to α variation than any atomic system studied before. Additionally, high Z also implies that these frequencies are less sensitive to external perturbations such as blackbody radiation, residual electric and magnetic fields, etc., making accurate measurements easier. Because californium is very heavy, Doppler shifts are reduced. In short, the relative systematics of this ion (systematics/signal) make Cf the best possible ion yet found for performing high-precision studies of α variation.

Method.—To find the $6p - 5f$ crossing, we start with neutral thallium. In thallium, the $5f$ orbital energies lie above the $6p$ orbitals, whereas in the large Z limit the $5f$ levels should be more tightly bound than $6p$ levels ($E_{5f} \approx E_{5p}$ for hydrogen-like ions). Therefore, we expect a level crossing at some $Z > 81$, where an ion may have optical transitions between these two orbitals. Figure 1 shows the Dirac-Fock energies of the $6p_{1/2}$, $6p_{3/2}$, $5f_{5/2}$, and $5f_{7/2}$ orbitals as a function of nuclear charge Z. Due to the large fine-structure splitting of the $6p_{1/2}$ and $6p_{3/2}$ subshells, there are two possible crossing points we can explore here, one for $6p_{3/2}$ near $Z = 93$ and one for $6p_{1/2}$ near $Z = 98$. The crossing near $Z = 98$ is more attractive for studying α variation for two reasons. First, the nuclear charge and ionization energy are larger. Second, since α sensitivity is due to relativistic effects that occur near the origin, the $6p_{1/2}$ orbital has larger q than the $6p_{3/2}$ orbital since the former has a lower Dirac-spinor component of $s_{1/2}$ symmetry, which is large near the origin. This is seen in Eq. (2) by the factor $1/(j + 1/2)$: the difference in q values due to this factor is greater for $p_{1/2}$ and $f_{5/2}$. Because the $6p_{1/2}$ level is highly sensitive to α variation while the $5f$ levels are not, we expect a large q value for a transition between these levels.

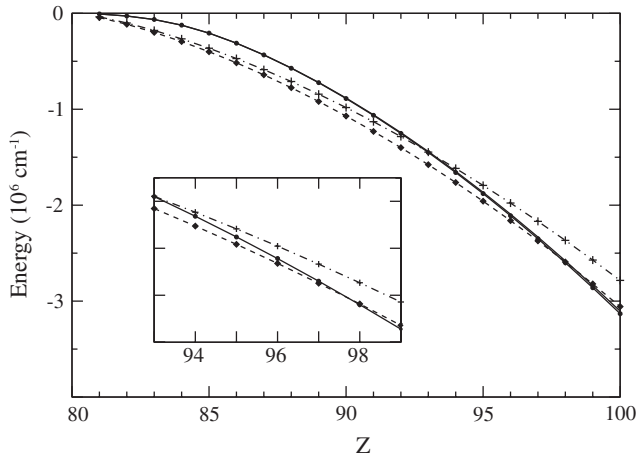

FIG. 1. Dirac-Fock energies of the $6p_{1/2}$ (diamonds, dashed line), $6p_{3/2}$ (crosses, dot-dashed line), and $5f$ (circles, solid line) levels in the thallium isoelectronic sequence with increasing nuclear charge. The inset shows an enlarged view of the crossing region.

We have performed full-scale *ab initio* calculations for Cf^{17+} (at the crossing point of Fig. 1) and the two-valence-electron equivalent Cf^{16+}. We use the combined configuration interaction and many-body perturbation theory method (CI + MBPT), presented in detail in Ref. [16] (see also Ref. [17]). We begin with Dirac-Fock for closed shells of Hg; this corresponds to V^{N-1} for the single-valence-electron case, Cf^{17+}, and V^{N-2} for the Cf^{16+} ion. From the frozen-core potential we generate a set of around 40 B splines in each wave up to $l = 6$. These form a "complete" set of virtual orbitals with which we calculate many-body perturbation theory (MBPT) corrections, Σ, to second order in the residual Coulomb interaction. For Cf^{16+} we perform a configuration interaction (CI) calculation including all two-electron excitations to the virtual orbitals $16spdf$. The addition of g-wave orbitals to the CI were found to make little difference to energy levels and q values. The q values were obtained by varying x [Eq. (1)] in steps of 0.01 and taking the gradient of transition frequency with respect to x.

The effect of quantum electrodynamic (QED) corrections on the energies and q coefficients has been calculated using the radiative potential method developed in Ref. [18]. The leading radiative corrections are of the order $\Delta E_r \sim \alpha^3$, which implies that the q coefficients are modified by $\Delta q_r = \frac{3}{2}\Delta E_r$ ($\lesssim 1000$ cm^{-1}). This means that even if the effect of QED corrections on the energy intervals might be noticeable (because the intervals are small), QED corrections to the q values are negligible.

We have also calculated some important transition rates (reduced matrix elements and Einstein A coefficients) using a relativistic formalism (see e.g., Ref. [19]). Random phase approximation corrections to the matrix elements were not included in this work since the uncertainty in the rates is dominated by uncertainty in the transition energies, which have not been measured.

Results and discussion.—Our calculated energy levels and q values for Cf^{17+} are presented in Table I. For the purposes of measuring α variation using atomic clocks, the most interesting transition is from the $5f_{5/2}$ ground state to $6p_{1/2}$, with an energy interval of $\omega = 17\,889$ cm^{-1}. The value of q for this transition is over eight times greater than the Hg^+ clock transition used in Ref. [7].

TABLE I. Low-lying levels of Cf^{17+} (all have odd parity). Energy calculations are presented relative to the $5f_{5/2}$ ground state using only Dirac-Fock (DF), including MBPT (DF + Σ) and QED corrections (DF + Σ + ΔE_r). The q values were calculated using DF + Σ.

		Energy (cm^{-1})			
Configuration	J	DF	DF + Σ	DF + Σ + ΔE_r	q (cm^{-1})
$5f$	5/2	0	0	0	0
$6p$	1/2	8447	17 889	18 686	−449 750
$5f$	7/2	20 447	21 755	21 848	17 900
$6p$	3/2	233 514	241 970	242 811	−115 650

In Cf^{16+}, presented in Table II, there are more states in optical range, arising from the greater number of angular momentum combinations available. Note that the levels marked A, A^* in Table II are heavily mixed in the CI calculation, resulting in a dominant contribution from $5f^2$ (63 and 51%, respectively) in both, while in the CI + Σ calculation the first state is 96% $5f^2$ and the second state is 63% $5f6p$. For simplicity, we have simply labeled the level with the largest $5f6p$ contribution as the $5f6p$ state.

Our CI-only calculations showed the $6p^2(J = 0)$ level to be the ground state, but adding MBPT corrections changes the level ordering such that $5f6p(J = 3)$ is the ground state. Actually, Cf^{16+} can be considered to have two ground states, since the decay from the metastable $6p^2(J = 0)$ ($G2$ in Table II) to the ground state ($G1$) has a lifetime greater than that of the nucleus itself. Table III lists calculated matrix elements and strengths for some transitions of interest.

TABLE II. Calculated energy levels, g factors, and q values for low-lying levels of Cf^{16+} (all have even parity) relative to the ground state $5f6p(J = 3)$. Energies are calculated using only configuration interaction (CI) and including many-body perturbation theory effects (CI + Σ). The ID column provides a convenient label reference in the text.

				Energy (cm^{-1})		
Configuration	J	ID	g	CI	CI + Σ	q (cm^{-1})
$5f6p$	3	$G1$	0.8299	0	0	0
$6p^2$	0	$G2$		−7429	5267	−370 928
$5f6p$	2		0.8482	7313	6104	106 124
$5f^2$	4	A	0.8535	28 746	9711	414 876
$5f6p$	4	A^*	1.0481	21 415	24 481	162 126
$5f^2$	2		0.7532	38 674	24 483	354 444
$5f6p$	3		1.1776	23 979	25 025	59 395
$5f^2$	5		1.0333	43 097	29 588	451 455
$5f^2$	3		1.0954	50 953	37 467	393 755
$5f^2$	4		1.1197	53 229	42 122	319 216
$5f^2$	6		1.1371	57 220	44 107	459 347
$5f^2$	0	B		68 192	51 425	380 986
$5f^2$	2		1.1672	67 267	51 471	446 045
$5f^2$	4		1.1198	69 475	58 035	461 543
$5f^2$	1	C	1.5000	75 018	58 132	449 977
$5f^2$	6		1.0296	78 739	63 175	460 416
$5f^2$	2		1.2672	89 580	75 041	465 293
$5f^2$	0			127 521	114 986	446 376
$5f6p$	3		0.9765	211 414	212 632	323 435
$6p^2$	1		1.4963	198 879	213 864	−113 277

The two electron transitions between the $G2$ metastable state and the $5f^2$ states give maximal values of q: up to around ∼830 000 cm^{-1}. Among these is the transition to $5f^2(J = 1)$ (C in Table II) with energy $\omega = 58\,132 - 5267 = 52\,865$ cm^{-1}, which has a very high branching ratio back to the $G2$ "ground" state. This level therefore potentially provides a method to "recycle" from $G1$ back to $G2$, although it should be noted that the $G1 \rightarrow C$ transition is rather weak.

Another very interesting potential reference transition is the $G2(J = 0) \rightarrow B(J = 0)$ transition at $\omega = 46\,158$ cm^{-1}, which is strongly forbidden but could be opened using Stark amplitude or hyperfine mixing of state $B(J = 0)$ with C ($J = 1$). Such a transition would be very narrow and have strongly reduced systematic shifts, e.g., electric quadrupole, ac Stark, Zeeman shifts. It may, however, be too weak to excite by usual optical lasers.

All of the transitions discussed so far are positive shifters: the transition frequency increases with increasing α. It is also possible to find negative shifters in Cf^{16+}; for example, the transition between $G1$ and $G2$ is a strong negative shifter (assuming that the ordering of levels has been calculated correctly). However, this transition is extremely weak, and in practice may only occur via level mixing using a strong laser. A negative shifter which may be more useful is from the $5f^2(J = 4)$ metastable state (A in Table II; lifetime $\sim 10^{-1}$ s) via $M1$ transition to one of the $5f6p$ states above it. The larger of these has $q = -355000$ cm^{-1}.

Systematics and opportunities.—HCIs have some interesting features that are worth mentioning here. First, electric dipole matrix elements are much smaller in HCIs than in neutral atoms since the $E1$ matrix element $\sim\langle r\rangle \sim \langle a_0/Z_{\rm eff}\rangle$, where a_0 is the Bohr radius and $Z_{\rm eff} \approx Z_{\rm ion} + 1$ is the effective nuclear charge: the charge that the valence electron sees. Since the spacing between $E1$ levels in HCIs is greater by a factor $\sim Z_{\rm eff}^2$, the static polarizability—and hence blackbody radiation shift—of HCIs is reduced compared to near-neutral ions by a factor $\sim 1/Z_{\rm eff}^4$.

The hyperfine structure in heavy HCIs is much larger than that in neutral atoms, scaling as $\omega_{\rm hfs} \sim ZZ_{\rm eff}^2$. The rate of $M1$ transitions within each hyperfine multiplet will scale as $\omega_{\rm hfs}^3$, which means that the lowest hyperfine state will be produced in reasonable time (order of a second). In californium, the hyperfine splitting of an s-wave or $p_{1/2}$-wave valence electron will be very sensitive to α variation because of the large Z. We define the fractional (relative) sensitivity $K_{\rm rel}$ by $\delta\omega_{\rm hfs}/\omega_{\rm hfs} = K_{\rm rel}\delta\alpha/\alpha$.

TABLE III. q values, squared reduced transition matrix elements S, and corresponding Einstein A coefficients for transitions between selected states i and k in Cf^{16+}. The included $6p^2$ state is metastable with respect to spontaneous decay into the ground state.

Configuration	J_i	$E_i(\mathrm{cm}^{-1})$	Configuration	J_k	$E_k(\mathrm{cm}^{-1})$	$q_{ik}(\mathrm{cm}^{-1})$	S	$g_k \cdot A_{ki}(\mathrm{s}^{-1})$
$5f6p$	3	0	$6p^2$	0	5267	−370 928	$0.924\,01_{M3}$	4.3519×10^{-18}
			$5f6p$	2	6104	106 124	$0.145\,53_{M1}$	0.892 81
			$5f^2$	4	9711	414 876	$0.168\,95_{M1}$	4.1731
			$5f6p$	4	24 481	162 126	2.5836_{M1}	1022.5
			$5f^2$	2	24 483	354 444	$0.004\,1938_{M1}$	1.6601
			$5f6p$	3	25 025	59 395	$0.071\,521_{M1}$	30.235
			$5f^2$	3	37 467	393 755	$0.063\,566_{M1}$	90.182
			$5f^2$	4	42 122	319 216	1.1631_{M1}	2344.7
			$5f^2$	2	51 471	446 045	$0.008\,2138_{M1}$	30.211
			$5f^2$	4	58 035	461 543	$0.139\,84_{M1}$	737.27
			$5f^2$	1	58 132	449 977	$0.002\,3199_{E2}$	0.172 49
			$5f^2$	2	75 041	465 293	$0.003\,6215_{M1}$	41.278
$6p^2$	0	5267	$5f6p$	2	6104	477 052	$0.541\,23_{E2}$	2.4845×10^{-8}
			$5f^2$	2	24 483	725 372	$0.019\,556_{E2}$	0.005 7377
			$5f^2$	2	51 471	816 973	$0.020\,833_{E2}$	0.49 127
			$5f^2$	1	58 132	820 905	0.1195_{M1}	476.2
			$5f^2$	2	75 041	836 221	$0.000\,71052_{E2}$	0.131 59
$5f6p$	2	6104	$5f^2$	4	9711	308 752	0.1839_{E2}	1.2569×10^{-5}
			$5f6p$	3	25 025	−46 729	3.1428_{M1}	574.24
			$5f^2$	1	58 132	343 853	$0.008\,2881_{M1}$	31.485
$5f^2$	4	9711	$5f6p$	4	24 481	−252 750	1.605_{M1}	139.5
			$5f^2$	2	24 483	−60 432	1.5203_{E2}	0.119 78
			$5f6p$	3	25 025	−355 481	$0.096\,413_{M1}$	9.3407
			$5f^2$	5	29 588	36 579	8.3595_{M1}	1771.0
$5f6p$	4	24 481	$5f6p$	3	25 025	−102 731	$0.995\,02_{M1}$	0.004 3219
$5f^2$	2	24 483	$5f^2$	1	58 132	95 533	$0.024\,099_{M1}$	24.766
$5f^2$	0	51 425	$5f^2$	1	58 132	68 991	1.6793_{M1}	13.671
$5f^2$	2	51 471	$5f^2$	1	58 132	3932	1.0698_{M1}	8.5301

Using formulas presented in Refs. [20,21], we obtain $K_{\mathrm{rel}} = 5.33$. Therefore, the hyperfine transitions form another positive shifting transition that can be used to place limits on α variation.

Conclusion.—In this Letter, we used the CI + MBPT method to calculate the energy levels for Cf^{16+} and Cf^{17+} highly charged ions. These ions were chosen because they lie at the $5f - 6p_{1/2}$ crossing point on the thallium isoelectronic sequence, which allows for optical transitions between different configurations from the ground state. Our calculations have identified several transitions in Cf^{16+} that have the largest q values ever seen in such atomic systems and include several positive shifters (with q up to $\sim 830\,000\ \mathrm{cm}^{-1}$) and negative shifters [e.g., $5f^2(J=4) \rightarrow 5f6p(J=3)$ with $q = -355\,000\ \mathrm{cm}^{-1}$]. A comparison of clocks using these reference transitions would have a total sensitivity $\Delta q = q_+ - q_- \approx 12\,00\,000\ \mathrm{cm}^{-1}$, around 23 times more sensitive than the Hg^+ clock and Al^+ clock comparison used to obtain the best current laboratory limit on α variation.

Trapping and cooling of HCIs remains a difficult experiment; however, electron-beam ion trap technology continues to improve [22–26], and we hope that the potential benefits of californium clocks will continue to motivate further studies.

This work was supported by the Australian Research Council and NCI National Facility. We thank Piet Schmidt for useful discussions.

[1] J. K. Webb, J. A. King, M. T. Murphy, V. V. Flambaum, R. F. Carswell, and M. B. Bainbridge, Phys. Rev. Lett. **107**, 191101 (2011).
[2] J. A. King, J. K. Webb, M. T. Murphy, V. V. Flambaum, R. F. Carswell, M. B. Bainbridge, M. R. Wilczynska, and F. E. Koch, Mon. Not. R. Astron. Soc. **422**, 3370 (2012).
[3] J. K. Webb, V. V. Flambaum, C. W. Churchill, M. J. Drinkwater, and J. D. Barrow, Phys. Rev. Lett. **82**, 884 (1999).
[4] M. T. Murphy, J. K. Webb, and V. V. Flambaum, Mon. Not. R. Astron. Soc. **345**, 609 (2003).
[5] M. T. Murphy, V. V. Flambaum, J. K. Webb, V. A. Dzuba, J. X. Prochaska, and A. M. Wolfe, Lect. Notes Phys. **648**, 131 (2004).
[6] J. C. Berengut and V. V. Flambaum, Europhys. Lett. **97**, 20006 (2012).

[7] T. Rosenband, D. B. Hume, P. O. Schmidt, C. W. Chou, A. Brusch, L. Lorini, W. H. Oskay, R. E. Drullinger, T. M. Fortier, J. E. Stalnaker, S. A. Diddams, W. C. Swann, N. R. Newbury, W. M. Itano, D. J. Wineland, and J. C. Bergquist, Science **319**, 1808 (2008).
[8] V. A. Dzuba and V. V. Flambaum, Phys. Rev. A **77**, 012515 (2008).
[9] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. A **59**, 230 (1999).
[10] J. C. Berengut, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. Lett. **105**, 120801 (2010).
[11] J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong, Phys. Rev. Lett. **106**, 210802 (2011).
[12] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. Lett. **82**, 888 (1999).
[13] A.-T. Nguyen, D. Budker, S. K. Lamoreaux, and J. R. Torgerson, Phys. Rev. A **69**, 022105 (2004).
[14] A. Cingöz, A. Lapierre, A.-T. Nguyen, N. Leefer, D. Budker, S. K. Lamoreaux, and J. R. Torgerson, Phys. Rev. Lett. **98**, 040801 (2007).
[15] O. Y. Andreev, L. N. Labzowsky, G. Plunien, and G. Soff, Phys. Rev. Lett. **94**, 243002 (2005).
[16] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).
[17] J. C. Berengut, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **73**, 012504 (2006).
[18] V. V. Flambaum and J. S. M. Ginges, Phys. Rev. A **72**, 052115 (2005).
[19] W. R. Johnson, *Atomic Structure Theory* (Springer, New York, 2007).
[20] J. D. Prestage, R. L. Tjoelker, and L. Maleki, Phys. Rev. Lett. **74**, 3511 (1995).
[21] V. V. Flambaum and A. F. Tedesco, Phys. Rev. C **73**, 055501 (2006).
[22] I. Draganić, J. R. Crespo López-Urrutia, R. DuBois, S. Fritzsche, V. M. Shabaev, R. S. Orts, I. I. Tupitsyn, Y. Zou, and J. Ullrich, Phys. Rev. Lett. **91**, 183001 (2003).
[23] V. Mäckel, R. Klawitter, G. Brenner, J. R. Crespo López-Urrutia, and J. Ullrich, Phys. Rev. Lett. **107**, 143002 (2011).
[24] J. R. Crespo López-Urrutia, Can. J. Phys. **86**, 111 (2008).
[25] M. Hobein, A. Solders, M. Suhonen, Y. Liu, and R. Schuch, Phys. Rev. Lett. **106**, 013002 (2011).
[26] P. Beiersdorfer, Phys. Scr. **T134**, 014010 (2009).